Muon-Spin-Rotation study of yttria-stabilized zirconia (ZrO$_2$:Y): Evidence for muon and electron separate traps

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Abstract. This paper is part of an extended study of oxide materials with the μSR technique. As an example, we present here experimental data on yttria-stabilized zirconia (ZrO$_2$ doped with 8% Y$_2$O$_3$). Three different muon states can be distinguished: i) Deep muonium (less than 17(1)% fraction), seen as a fast-relaxing signal or indirectly via decoupling measurements in high longitudinal fields, ii) μ^+ in a paramagnetic environment 62(6)% fraction), characterized by a very weak but clearly-visible hyperfine interaction, and iii) diamagnetic muon 21(1)% fraction); the diamagnetic signal is broadened only by the interaction with nuclear moments. The state corresponding to μ^+ in a paramagnetic environment and the diamagnetic state are attributed to the same (oxygen-bound) muon configuration, but we assume that they have different electron surroundings (with or without an unpaired electron in the vicinity). The paramagnetic electron is not captured in the Coulomb potential of the positive muon but is self-trapped (polaron formation) at a nearby Zr ion. The distant electron interacts with the muon only via dipolar magnetic fields. This explains the very weak hyperfine interaction felt by the μ^+ state in a paramagnetic environment. A further result of the experiment is that the disappearance of this signal with increasing temperature is not due to ionization of an electron shallowly bound to the muon but is caused by rapid spin fluctuations of the electron, averaging the hyperfine interaction to zero.

1. Introduction

Zirconia is used in a multitude of devices such as oxygen sensors [1], thermal barrier coatings [2], medical prostheses [3], gate oxide material [4, 5], solid oxide fuel cells [6], cladding material for nuclear reactors [7]. In this material, protonated forms can occur in the conspicuous presence of hydrogen, and that might play an important role in the use of ZrO$_2$ in the last three applications mentioned. Muonium spectroscopy has now become a standard technique in order to investigate hydrogen configurations through modelling with muonium, a light pseudo isotope of hydrogen [8]. In μSR experiments on chalcogenides and oxides [9, 10, 11, 12, 13, 14, 15] one often finds

a muonium state with a rather small hyperfine interaction. This signal is sometimes directly identified spectroscopically through the frequencies corresponding to the hyperfine interaction [9, 10, 11]. However, in many cases these lines are not resolvable and only a broad diamagnetic line is visible, with a temperature dependent relaxation larger than that expected from nuclear broadening alone [16, 15, 13, 14, 12]. These signals disappear at low temperatures between about 20 and 50 K. The usual interpretation is that a shallow muonium state is formed in the screened Coulomb potential of the muon. The ionization energy and the contact hyperfine interaction correspond roughly to the calculated values for a hydrogen-like atom with an effective-mass electron and a dielectric medium.

In our experiments in yttria-stabilized zirconia (and other oxide materials) we find severe deviations from this model: The hyperfine interaction is extremely small (only about 50 kHz) and not unique and the paramagnetic signal persists up to rather high temperatures (150 K and higher in some cases). These findings are inconsistent with the shallow-donor concept and require a different interpretation. Recent theoretical calculations [17] show that in these materials the paramagnetic electron is not localized on the oxygen-bound muon but is concentrated on a Zr cation some distance away from the muon. The corresponding single electron energy level lies about 1 eV below the conduction band indicating a rather strong binding energy. This concept of a separate localization of the electron and the muon gives a consistent interpretation of the present experimental data. Yttria-stabilized zirconia has been investigated before and the data have been published [14]. However, the analysis and the interpretation of these earlier measurements were not clear and many questions were left over. We felt that new and more precise data were necessary to solve the open problems. The main result of the present paper is a new interpretation of the paramagnetic signal. We show that it arises from a self-trapped electron in the vicinity of the muon.
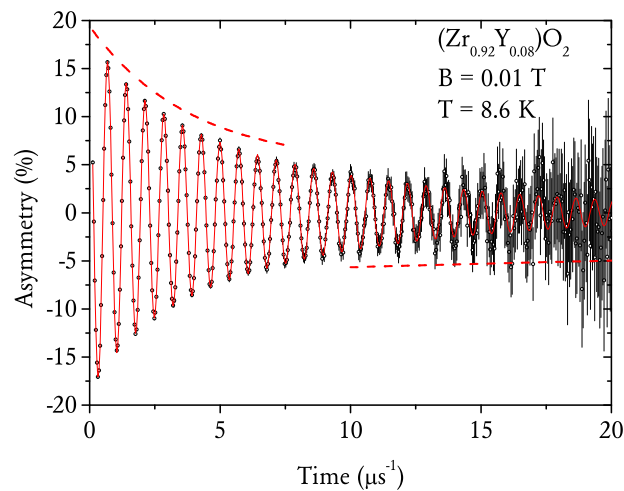
Figure 1. μSR time spectrum of $Zr_{0.92}Y_{0.08}O_2$ measured at ISIS in the transverse geometry, for an external magnetic field $B = 0.01$ T and a temperature $T = 8.6$ K. An oscillation at the Larmor frequency ($\nu = 1.355$ MHz) is observed. The spectrum is decomposed in two components (f_{para} and f_{dia}) with slightly different relaxations, as discussed in the text. Dashed lines show the respective trends $f_{para} \exp(-\lambda_{para} t)$ (above) and $f_{dia} \exp(-\lambda_{dia} t)$ (below). The very-fast relaxing component (deep muonium) is not observed in this experiment.

2. Experimental details

The muon-spin rotation experiments took place at the EMU instrument of the ISIS Facility, Rutherford Appleton Laboratory, United Kingdom. A nanocrystalline $(Zr_{0.92}Y_{0.08})O_2$ sample (grain size 17 nm) kindly provided by Innovnano was investigated. In the experiments, 4 MeV positive muons were implanted into the sample, and transverse-field measurements at an external magnetic field of 0.01 T were undertaken in the temperature interval 8.6 K to 600 K. Repolarisation measurements in the longitudinal geometry were also undertaken at room temperature (300 K). A calibration of the maximum instrumental asymmetry was performed with a silver sample. Data analysis was done using the WiMDA program [18]

3. Experimental results and analysis

Figure 1 shows the 8.6 K transverse-field time spectrum. In this experiment the presence of a fast-relaxing component is observed indirectly from a missing fraction of the muon spin polarisation. After comparison with the maximum instrumental asymmetry obtained with silver, the missing fraction, corresponding to the fast component, is 17(1)% at this temperature.

The main feature of the spectrum in figure 1 is an oscillation at the Larmor frequency corresponding to the external transverse magnetic field of 0.01 T. An analysis of the spectrum with a single relaxing component (using Lorentian, Gaussian, or Abragam relaxation functions) does not give an acceptable fit (typical χ^2 values are around 2.5). We therefore decomposed the spectrum $P(t)$ into two fractions (f_{para} and f_{dia}) with slightly different relaxations (λ_{para} and λ_{dia}):

$$P(t) = f_{para} \exp\left(-\lambda_{para}\, t\right) \cos\left(\omega t + \phi\right) + f_{dia} \exp\left(-\lambda_{dia}\, t\right) \cos\left(\omega t + \phi\right) \tag{1}$$

The angular frequency ω and the phase ϕ were assumed to be the same for the two fractions. The indices dia and $para$ stand for diamagnetic and for μ^+ in a paramagnetic environment, respectively.

We used exponential decay functions because of mathematical reasons since the relaxations are additive if two mechanisms contribute to the relaxation. This is the case for the fraction of μ^+ in a paramagnetic environment, where electronic and nuclear interactions exist. If at higher temperatures the electronic interaction disappears, the nuclear part remains. In principle, a Gaussian function should be used for the nuclear part of the relaxation if this is the only interaction. But this leads to mathematical problems when two interactions (electronic and nuclear) exist at the same time. Thus choosing a Lorentzian function for the nuclear relaxation has practical reasons. The error introduced by this choice is not too severe since, at low temperatures, it concerns only the correction part of the relaxation but not the main component.

A fit with all parameters free did not give satisfactory results because of too many ambiguities. In particular at higher temperatures where the two components merge together, no clear separation was possible. We therefore used the following strategy: we first fitted the spectrum at 8.6 K with all parameters free, except λ_{dia} which was fixed to 0.03 μs^{-1}. From this fit we obtained a formation probability of the diamagnetic fraction $f_{dia} = 21(1)\%$, a fraction $f_{para} = 62(6)\%$ of μ^+ in a paramagnetic environment, and $\lambda_{para} = 0.29(1)\mu s^{-1}$, all at 8.6 K. We than assumed that the fractions do not change in the low temperature range and fitted the rest of the data with only λ_{para} as a free parameter. The results are shown in Fig. 2.

The longitudinal-field data obtained at room temperature were fitted using $P(t) = f_{dia} \exp\left(-\lambda_{dia}\, t\right)$ since at that temperature the λ_{para} relaxation is practically the same as λ_{dia}.
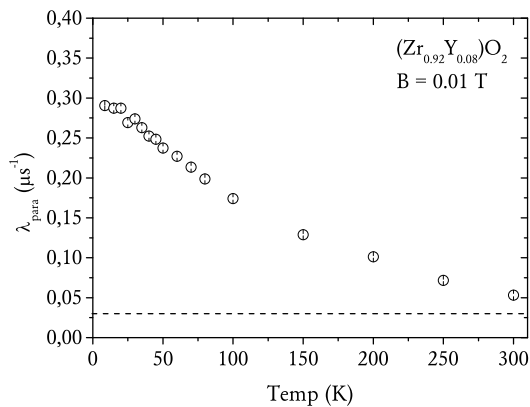
Figure 2. Temperature dependence of the relaxation rate λ_{para} of the component corresponding to μ^+ in a paramagnetic environment. The value of the corresponding fraction f_{para} is given in the insert of the figure. The transverse magnetic field was 0.01 T. The dashed line at 0.03 μs^{-1} corresponds to the estimated dipolar width caused by ^{91}Zr and ^{89}Y nuclei.

4. Discussion

4.1. Deep muonium state

The 17(1)% fast-relaxing component is attributed to the formation of deep interstitial muonium centers at or near the surface of the nano-grains. An alternative interpretation is that muonium formation occurs in the bulk of the grains, despite the higher strain in the nano-crystals compared to samples with large grains. The strength of the hyperfine interaction for this muonium state is estimated to be around 2 GHz (about half the vacuum value) as derived from the decoupling curve in Fig.3. The interaction is possibly anisotropic. The line in figure 3 is a fit with an approximate analytical form for the repolarization of axially symmetrical muonium in a polycrystalline sample [19], yielding $A_{iso} = 2.1(1)$ GHz and $D = 0.129(15)$ GHz.
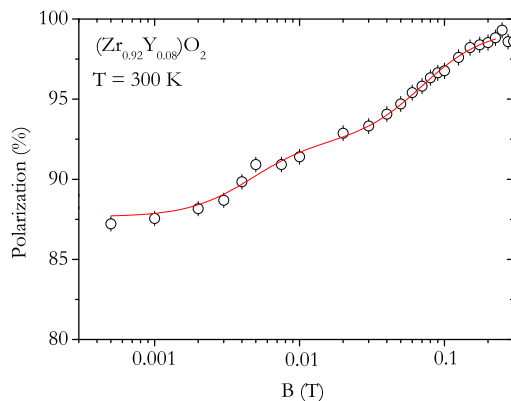

Figure 3. Repolarization curve at 300 K. The line is a fit with an approximate analytical form for the repolarization of axially symmetrical muonium in a polycrystalline sample [19], yielding $A_{iso} = 2.1(1)$ GHz and $D = 0.129(15)$ GHz.

4.2. μ^+ state in a paramagnetic environment

The 83(4)% slowly-relaxing signal is attributed to muons bound to oxygen (muoxyl μ-O similar to hydroxyl H-O). As described above, we divided this part into two fractions, 62(6)% corresponding to diamagnetic muons without the influence of electron relaxation, and 21(1)% to a μ^+ state in a paramagnetic environment. The relaxation of the latter component at low temperatures is almost an order of magnitude larger than the expected nuclear relaxation (about 0.03 μs^{-1}) and must therefore be due to an unpaired electron in the vicinity of the muon. However, the electron cannot be too close either, since this would cause a too strong interaction. Theoretical calculations by Marinopoulos [17] employing hybrid functionals show that the electron is likely

to be localized predominantly on a Zr cation 4 Å away from the H nucleus. These calculations demonstrate convincingly this separate localization of hydrogen (analogous for muon) and the electron (Fig. 4): the density distribution of the unpaired electron (in yellow) is not centered on hydrogen (red point) but is localized quite a distance away from it. Thus the contact hyperfine interaction is small (or zero) and the only remaining term is the very small dipolar interaction. The dipolar interaction being angle-dependent, a distribution of hyperfine splittings is expected in a polycrystalline sample. This picture explains the small, non-unique value of the hyperfine interaction observed in the experiment.

The relaxation λ_{para} has two contributions, one part λ_e due to the nearby electron, the other λ_n due to the magnetic field distribution caused by the surrounding nuclear moments: $\lambda_{para} = \lambda_e + \lambda_n$. The decrease with temperature is attributed to line narrowing due to electron spin fluctuations. This allows an estimate of the electron relaxation time T_1 [20, 21]. We obtain T_1-values in the order of 1 μs at 100 K. As far as we know, the value of T_1 for the corresponding T center observed in EPR measurements has not been measured and only T_1 values for the F center (electron trapped in an oxygen vacancy) are known ($T_1 = 7\mu$s at T=100 K) [22].
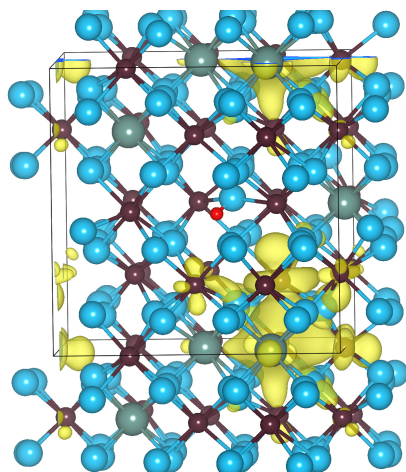
Figure 4. Calculated electron-density isosurface (in yellow) for the defect state of the neutral bond-type hydrogen (red point) configuration in yttria-stabilized zirconia. The unit cell, indicated by the cube, is repeated periodically [17].

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